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Dissolution of Poly(p-hydroxystyrene): Molecular Weight Effects

by

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ABSTRACT

In the present study, dissolution rates of PPHS films were measured in aqueous base solvents and in 4-methyl-2-pentanone (MIBK) using laser interferometry. Molecular weights from 6,000 to 100,000 were employed. The films (0.5 to 2 μm thick) were spun on silicon wafers from MIBK solutions and baked 1 hour at 160°C. The most striking feature of dissolution behavior is the peculiar way in which rate varies with molecular weight. Below a molecular weight of about 20,000, the rate decreases with molecular weight as one might expect. Above 30,000, the rate in aqueous base is much higher and seems to be almost independent of molecular weight. The behavior in MIBK, while more conventional, shows some of the same features. Another feature found with PPHS that is not usual with other polymers is a decrease in dissolution rate with increased thickness. Conventional wisdom would predict that retained solvents (after baking) in thick films would accelerate dissolution compared to thin films. Moreover, the interferograms for thick films show no pronounced change in dissolution rate as the film dissolves. Baking conditions and the pH of the aqueous base developer also affect the dissolution behavior.

1. INTRODUCTION

The dissolution process of phenolic resins is a central feature of many widely-used positive-working photoresist systems. Although most use low molecular weight alkylphenol-formaldehyde condensates (novolacs), an attractive alternative is poly(p-hydroxystyrene), abbreviated as PPHS (Fig. 1). Another name used for the same polymer is poly(vinyl phenol). The linear structure, and reproducible synthesis of PPHS makes it an attractive candidate for studies of the dissolution process. Novolacs generally are somewhat branched and often made from mixtures of substituted phenols so that generalizations are harder to make[1].

PPHS has been used in lithographic resists in several ways. However, it has not been successful as a straightforward replacement of conventional novolacs when compounded with a diazoquinone. Although the diazoquinone acts as a dissolution inhibitor for PPHS until exposed to UV light, PHHS has been found to dissolve too rapidly for practical purposes in the "inhibited" unexposed state compared to novolacs[1]. A negative resist from Hitachi uses a biazide compound for UV crosslinking[2].

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Willson[3] and others have worked with a readily-hydrolyzed derivative of PPHS, namely poly(p-tert-butyloxycarbonyloxystyrene), abbreviated as "t-BOC" [Fig. 1]. When an acid is generated by exposure to radiation (followed by heat treatment), the "t-BOC" is converted to PPHS. Since the former is non-polar and the latter is base-soluble, both positive and negative patterns can be developed depending on the choice of developing solvent.

In any of these resist systems, the dissolution behavior of PPHS can be very important. Thus it seems worthwhile to examine the effect of structural variables on the dissolution rate. In particular, the effect of molecular weight is of great interest. In most applications, the PPHS is not expected to change in molecular weight on exposure. Thus the criteria for selecting an optimum molecular weight can be based on factors other than the slope of the molecular weight-exposure dose curve.

2. EXPERIMENTAL PROCEDURES

PPHS samples varying in molecular weight were furnished by Michael Sheehan of the Hoechst-Celanese Corp. The molecular weights were estimated in several ways (Table 1). The first listed is a weight-average molecular weight based on column chromatography (GPC) results for the acetate esters appropriately weighted for the difference in repeat structure after hydrolysis. The second is based on GPC (tetrahydrofuran, THF, as solvent) for the PPHS itself. In either case, the molecular weight is a polystyrene-equivalent, not an absolute figure. In the last column are some intrinisc viscosity results. These were run in order to verify the GPC data. In column chromatography, interactions of polar polymers like PPHS with end fittings and packing sometimes lead to anomalous behavior. The viscosity measurements are less subject to such interference. The good correlation of intrinsic viscosity with the acetate-ester-based molecular weights increases confidence in their meaning [Fig. 2]. The equation corresponding to the straight line for solutions in THF at 30°C [Fig. 2] is

$$[\eta] = 2.84 \times 10^{-4} (M_w)^{0.665} \qquad (1)$$

where the intrinsic viscosity is expressed in gram/deciliter (g/dL). One conclusion is that THF is a relatively good solvent for PPHS. A poor ("theta") solvent would have an exponent of 0.5 and a very good solvent might have an exponent of 0.8. Another observation is that intrinisc viscosity values in methanol and in methyl isobutyl ketone (MIBK) are almost the same as in THF. That is not to say that properties of PPHS solutions are identical in all three solvents. Films formed from MIBK solutions are smooth and clear, while those from methanol or THF tend to be somewhat rough and hazy. For all of the dissolution tests, films were cast from MIBK onto silicon wafers and baked one hour at 160°C unless otherwise specified.

Dissolution rates were measured using the laser interferometer as described by Krasicky et al[4]. The reflection of a laser beam (632 nm) from the polymer-coated wafer submerged in developing fluid was

monitored with a photocell. A reflected light intensity pattern reveals the rate of dissolution (which can change as the film dissolves).

The solvent used for dissolution were MIBK and solutions of sodium hydroxide. In some tests (Fig. 10), a salt was added to the sodium hydroxide solution.

3. RESULTS AND DISCUSSION

3.1 Molecular Weight Dependence of Dissolution Rate

In most cases of non-polar polymers dissolving in organic solvents, the dissolution rate decreases regularly with increasing molecular weight. For example, Cooper[5] found that, for PMMA (poly(methyl methacrylate)), the slope for molecular weights less than 10,000 was about -2.5. When PPHS samples are developed in 4-methyl-2-pentanone (also called methyl isobutyl ketone, MIBK), a conventional dependence appears with no break [Fig. 3]. The leveling off of dissolution rate at higher molecular weights is similar to that of PMMA although the effect seems to set in at a lower molecular weight for PPHS than for PMMA.

The most striking feature of dissolution behavior in an aqueous developer is the peculiar way rate varies with molecular weight (Fig. 4). Below a molecular weight of about 20,000, the rate decreases with increasing molecular weight as one might expect. Above 30,000, the rate is much higher and seems to be almost independent of molecular weight.

Both Pampalone[1] and Hashimoto[2] reported a conventional decrease in dissolution rate with molecular weight for PPHS [Fig. 5]. The molecular weight range in either case was rather low. Moreover, in Pampalone's data, there appears to be a bottoming out of dissolution rate above M_w about 15,000. Hashimoto's samples were narrow in distribution ($M_w/M_n = 1.28$) while Pampalone's were broad ($M_w/M_n \sim 15$ to 73). The developers used differed, but the pattern of molecular weight dependence was strikingly similar to that for cresol novolac polymers[6] also shown in Figure 5. The slope in all three instances was on the order of -2.5.

The behavior of the higher molecular weights is not easily rationalized. The basic mechanism of dissolution does not appear to change discontinuously when the reflected light pattern during dissolution is examined. The reflected light pattern can be interpreted in terms of a transition layer (or a gel layer) increasing in size with molecular weight[4]. One measure of the size of the layer is the ratio of the offset, s, to the amplitude of the sinusoidal oscillation, Δx [Fig. 6]. The patterns for several molecular weights of PPHS at pH = 12.7 indicate a discernible layer at all molecular weights above the lowest [Fig. 6]. There is no obvious discontinuity in offset consistent with the discontinuity in dissolution rate, but the transition layer does, indeed, become larger at the molecular weights above 50,000.

One possible explanation for the constant rate of dissolution above a certain molecular weight is that there may be a fundamental change in the controlling step of the dissolving process. In order for the rate to be independent of polymer size, the rate of diffusion of base may control. It is well known that polymers change in mechanism of viscous flow at an "entanglement molecular weight". The easiest way to establish that point is by noting the point where power dependence of melt viscosity on molecular size changes from about unity to a value of about 3.5. For most polymers the entanglement (or critical) molecular weight corresponds to a chain length of a few hundred to a thousand chain atoms[7].

The discontinuity in dissolution rate may correspond to the entanglement molecular weight for PPHS. Perhaps dissolution becomes slower with increasing MW only so long as single molecules of the polymer are removed from the surface. However, when the entanglement point is reached, the polymer no longer packs into the solid phase as compactly. Under these circumstances, cations penetrate faster and entangled masses of polymer are removed. This picture is consistent with the thicker transition (or gel) layer observed. If we picture the polymer chains in terms of the number of chain atoms in each molecule (two chain atoms per monomer repeat unit), a configuration corresponding to an internally hydrogen-bonded micelle is consistent with molecular models (Fig. 7). Templeton et al[8] have remarked on the usefulness of molecular models for visualizing the position of the hydroxyl groups. However, above a molecular weight in the range of 300 to 400 chain atoms, we hypothesize that the compact arrangement becomes less stable and surface hydroxyl groups appear. Below the "critical chain length", dissolution is controlled by chain unfolding and removal which is controlled, in turn, by chain length. Hence, the usual decrease of dissolution rate with increasing molecular weight. Above the "critical chain length", the dissolution rate may be controlled by the reaction of the hydroxyls with the cation (say, Na^+). Thus, the heavy dependence on cation concentration, a decrease in rate with increased cation size, and almost no influence of chain length. It would be reassuring to find some other physical characteristic of the films that shows a discontinuity with increasing molecular weight at the "critical chain length". So far, no simple test has yielded such a result. Contact angle measurements of water on thin films of PPHS show no statistically significant difference over the range of 6,500 to 30,800. IR spectra and refractive index also show no consistent pattern of change with molecular weight.

3.2 Effect of pH

Most workers have commented on the sensitivity to pH of dissolution rate for both PPHS and novolacs. In the present study also, the rate appears to increase with the third or fourth power of base concentration [Fig. 8]. That is, for a completely ionized base like NaOH, $\log [Na^+] = (pH - 14)$. In a recent paper, Huang, et al [9] found that the dissolution of model novolac resins displayed rates that were proportional to sodium hydroxide concentration to a power in the range of 2.6 to 3.5 which is very similar to the present results. The dependence on pH does not seem to be affected strongly by molecular weight.

3.3 Effects of Film Thickness and Prebake Temperature

There appears to be a well-defined decrease in dissolution rate as film thickness increases [Fig. 9]. The effect is seen both in MIBK and in the aqueous developer. Ordinarily one would reason that the thicker films would contain more residual solvent, especially towards the polymer-wafer interface. However, the thinner films definitely dissolve more rapidly. Moreover, the rate of dissolution does not seem to change as the dissolution procedes from top to bottom of a thick film such as that illustrated in Fig. 6. That devolatilization occurs seems to be confirmed by the decrease in dissolution rate with prebake temperature up to about 160°C ([Fig. 10]. As one might expect, the lowest molecular weight is devolatilized more readily. However, there is also an apparent increase in rate when films are heated at higher temperatures. This is a somewhat misleading artifact, because films baked at much higher temperatures become crosslinked and partly insoluble. The increased rate is seen only for the uncrosslinked portion, but a residual film remains afterwards. The temperature of 160°C was selected because it was the highest baking temperature which gave completely soluble films for all the samples.

4. CONCLUSIONS

The dissolution of thin films of poly(p-hydroxystyrene) in aqueous base displays some anomalous behavior. The major anomaly is the lack of dependence of dissolution rate on molecular weight above a critical chain length of some 300 to 400 chain atoms. The formation of an internally bonded (and shielded) micelle at low molecular weights together with the increased availability of surface hydroxyl groups at high molecular weights is only a qualitative explanation and awaits further studies of film characteristics. The decreased rate with increased film thickness also is unexpected since it runs counter to the expected behavior with retained casting solvent in thick films. These anomalous effects have not been seen by us in a non-polar polymer like poly(methyl methacrylate) or even somewhat polar polymers like poly(vinyl chloride) and copolymers of maleic anhydride.

5. ACKNOWLEDGMENTS

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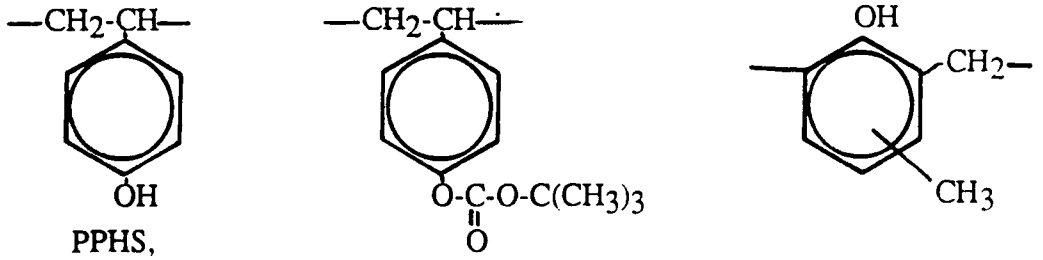
TABLE 1 Molecular Weights ($x10^{-3}$) of PPHS Samples

Based on GPC of acetate precursor	Based on GPC of PPHS directly in THF			Intrinsic viscosity in THF
M_w	M_n	M_w	M_w/M_n	[η], dL/g, 30°C
6.3	----	----	----	0.094
6.5	5.2	7.7	1.5	0.091
10.3	---	---	---	0.15
17.5	9.9	38	2.6	0.21
25.2	---	---	---	0.23
28.7	16.8	39	2.3	0.26
30.8	17.8	40	2.2	0.30
56.2	30.2	72	2.4	0.38
98.7	51.5	121	2.3	0.57

Fig. 1 Phenol-Based Polymers



PPHS, Poly(p-hydroxy styrene) | "t-BOC" | Typical novolac

Fig. 2 Correlation of Intrinisc Viscosity, [η], with Weight Average Molecular Weight, M_W.

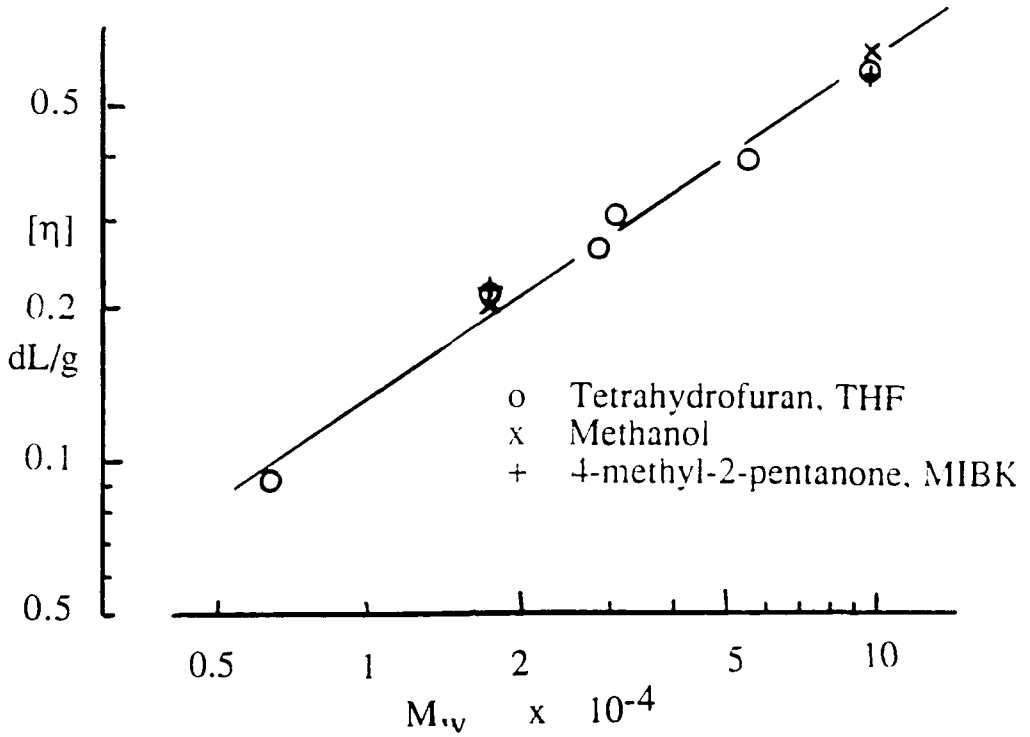


Fig. 3 Dissolution rates of PPHS films in MIBK.

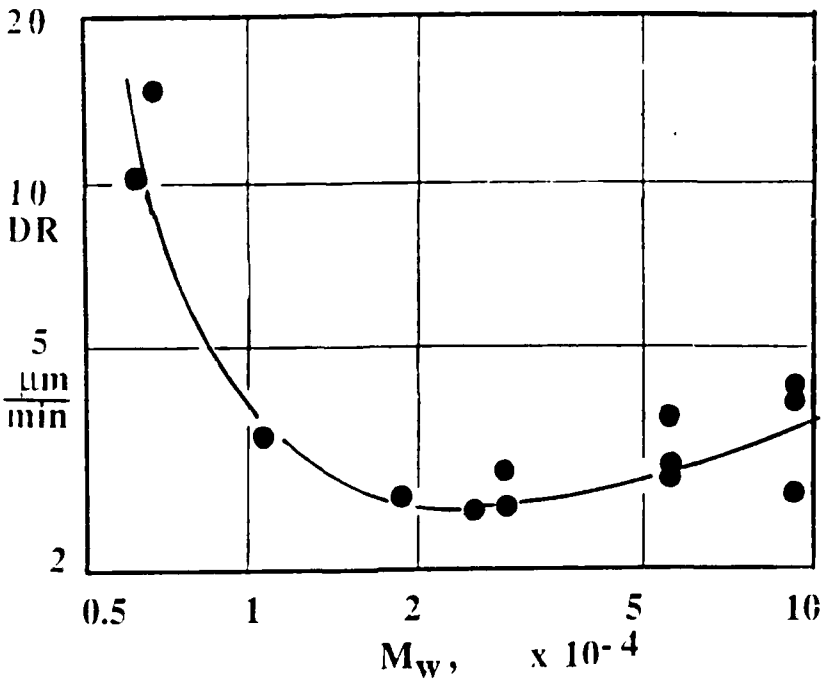


Fig. 4 Dissolution rates for PPHS in aqueous base (sodium hydroxide).

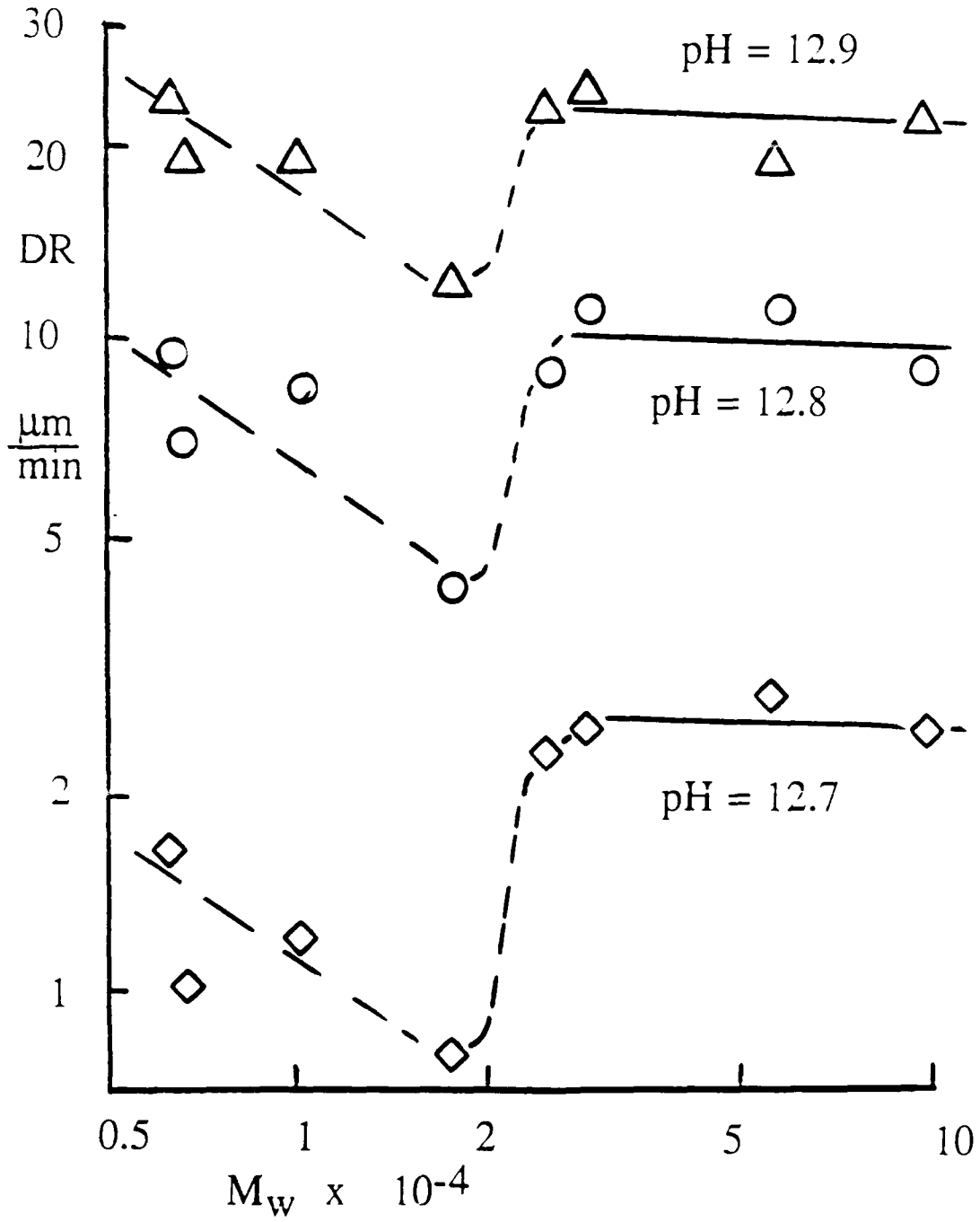


Fig. 5 Relative Dissolution Rates of Low Molecular Weight Polymers in Aqueous Media. PPHS, o (Ref. 2); ◆, (Ref. 1); x, (present work); and Novolac, Δ (Ref. 6). Rates have been normalized arbitrarily.

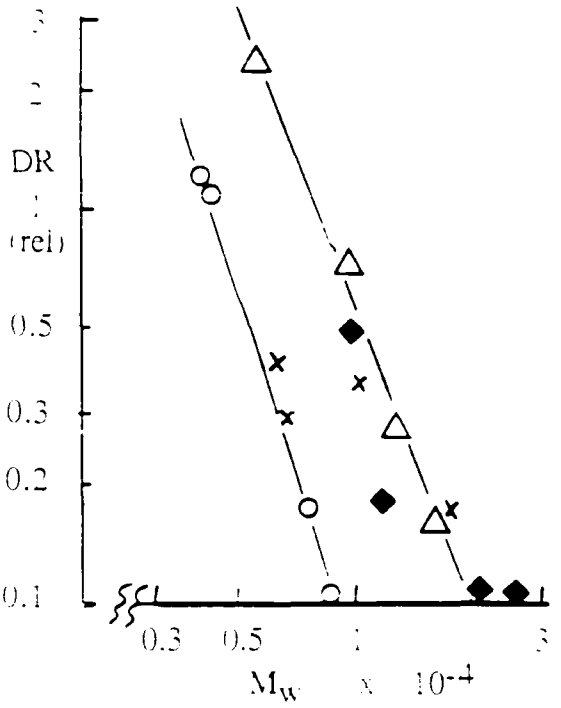


Fig. 6. Reflected light interferograms for dissolution in aqueous base at pH = 12.8 of PHHS of Mol. Wt. = 17.5×10^3 at two initial thicknesses, (b) 0.43 μm; (d) 2.1 μm; and for Mol. Wt. = (a) 6.5×10^3, 1.7 μm thick; and (c) 30.8×10^3, 0.62 μm thick.

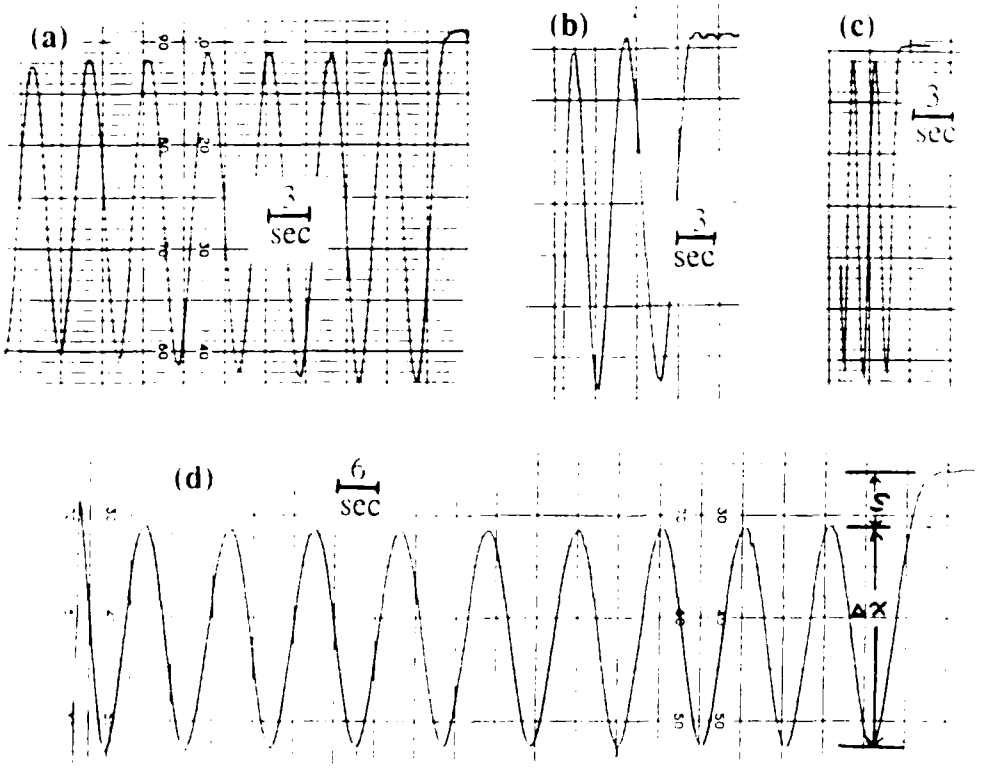
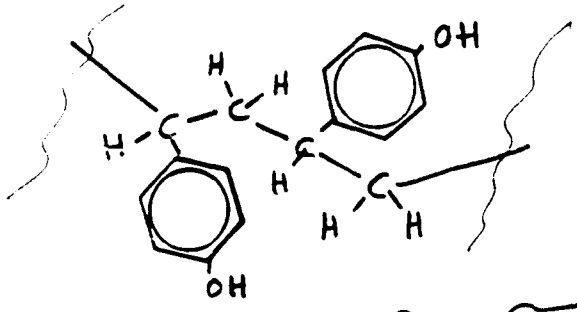
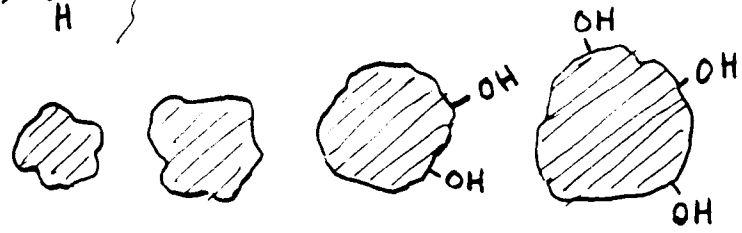


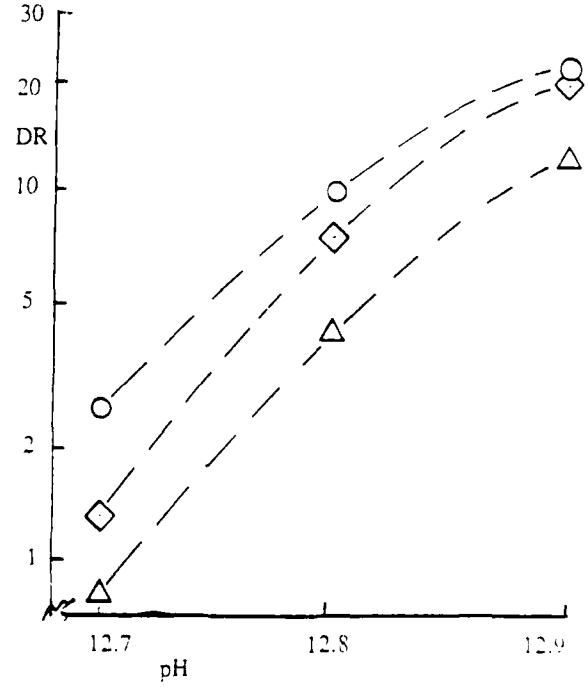
Fig. 7. A Micellar Model for the 3-dimensional PPHS Chain. The formula weight of each repeat unit (two chain atoms) is 120.





Postulated "Micelle" appearance				
Molecular Weight	6,000	18,000	36,000	72,000
Number of repeat units	50	150	300	600
Number of chain atoms	100	300	600	1,200
	Rate controlled by unfolding		Rate controlled by diffusion	

Fig. 8 Effect of pH on Dissolution Rates in Aqueous Base. o, MW = 100×10^3; Δ, MW = 17.5×10^3; ◊, MW = 8×10^3.



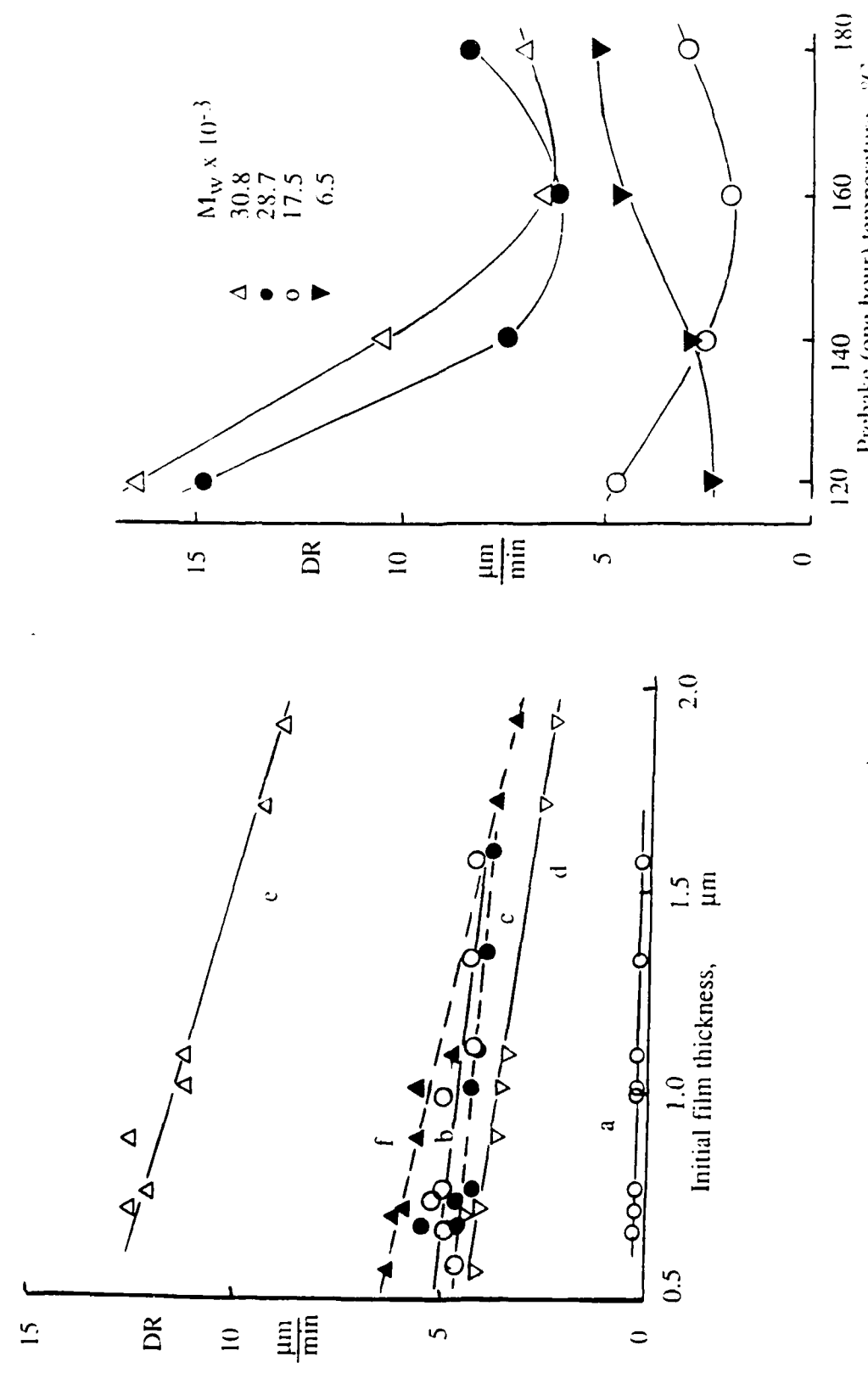


Figure 9. Dissolution Rate versus Initial Thickness. Circles, M_w = 17.5x10^3, (a) pH = 12.7, (b) pH = 12.8, (c) MIBK; triangles, M_w = 56.2x10^3, (d) pH = 12.7, (e) pH = 12.8, (f) MIBK.

Fig. 10. Effect of Prebake Temperature on Dissolution Rate. Developed at 23°C in pH= 12.85 sodium hydroxide (with tetramethylammonium chloride added).

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